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(54) CLEANING COMPOSITION

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a cleaning composition useful for releasing the particular soils that tend to accumulate in toilets and similar sanitary facilities.

While the precise chemical identity of such soils has not been completely determined, the soils themselves are well-known in the sanitation art and there are several types that are commonly encountered in the sanitary maintenance of toilet facilities.

In the professional maintenance of sanitary public facilities, probably the most troublesome of all is a hard, rock-like, white or nearly white deposit, which is some kind of reaction product from urine. This material tends to accumulate, even on apparently clean, smooth, glazed and polished surfaces such as the glazed interior porcelain surface of a toilet bowl, and adhere thereto so that removal by mechanical scraping is likely to cause damage to the glazed surface. Such mineral-like deposit is not smooth as was the glazed surface upon which it usually deposits, but provides an excellent site for other soils to accumulate, greatly compounding the problem of sanitation of public facilities. The problem is of the greatest severity when urine is deposited in a pool of water which also contains dissolved alkali metal or alkaline earth metal salts and is permitted to stand in contact with both such water and with the toilet bowl or urinal interior surface for a period of time prior to being removed by flushing. When, as in most domestic facilities, the toilet is flushed as regularly as it is used, the problem may appear but is of much less severity.

A second kind of soil which is frequently a problem in the management of sanitary facilities is closely adherent fecal matter. The problem is of greatest severity above the water pool which normally occupies the lower portion of a toilet bowl except in those instances when, below the water line, a deposit of urine-originating, rock-like solids is present to enhance adherence.

A third form of soil which is encountered in some situations is rust, which while not inherently objectionable, is unsightly and, as in the case of other adherent solids, provides a site for bacterial and fungal growth.

Such growth of microorganisms may constitute a severe soil problem. It is well-known that in unoccupied or unused facilities permitted to stand over a period of a few weeks without attention, a mat of microorganic material may form over the surface of the water pool.

For the removal of the hard, stone-like deposit from urine, the prior art routinely calls for the use of a mineral acid, and hydrochloric acid is frequently preferred. Sometimes nitric acid is used because of the greater solubility of some nitrates than of the corresponding chlorides.

For the removal of securely adherent and perhaps dried fecal matter, scraping together with surfactant scrubbing with a brush are the most widely recommended and commonly preferred methods. For the control of accumulation of rust, no very good method is known. A toilet bowl can be emptied of water and washed with a mineral acid to remove rust. This is laborious and uses hazardous materials. For the removal of closely adherent, microbiological substances, mechanical scrubbing with a brush is sometimes favored; control is sometimes attempted by dropping into the tank of those

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flush toilets equipped with a water tank a block of paradichlorobenzene or some comparable mild germicidal substance.

It has now been discovered that a combination of solvent and related materials, in combination, solubilizes for almost effortless removal the stone-like deposit from reaction of urine, dried closely adherent fecal matter, and gelatinous microorganisms, while maintaining rust-free, or nearly so, a toilet surface used in an exposure situation conducive to the accumulation of rust. The cleaning composition in question has some limited capacity to remove rust, but is much more effective for maintenance of a rust-free situation.

According to the present invention there is provided an aqueous cleaning composition of a pH of from 7 to 12, comprising a chelating agent in the amount of from 0.25 to 15 parts; a loweralkanol of from 1 to 4 carbon atoms in the amount of from 1 to 5 parts; an alkanolamine of which any alkanol moiety is of from 2 to 4 carbon atoms and there are from 1 to 3 such alkanol moieties per molecule, and the alkanolamine is in the amount of from 0.8 to 6 parts; and a mixture of two or more different loweralkyl ether alcohols of which each is terminated on one end by an alkyl group of from 1 to 4 carbon atoms, ether bonded through oxygen to an alkylene moiety of from 2 to 4 carbon atoms, said alkylene moiety being terminated by a hydroxyl group, each such loweralkyl ether alcohol being present in an amount of from 1 to 5 parts; all amounts being by weight and all parts being by weight of 100 parts of total composition, water being present in amount to complete said composition to 100 weight parts.

Additionally, and sometimes desirably, there may be present other substances which cooperate with and enhance the total performance of the composition, such as a surfactant, a germicide.

For the purposes of the present invention, suitable chelating agents include nitrilouriacetic acid, ethylenediaminetetraacetic acid, the polyalkylenepolyamine polyaliphatic polylower acid substances generally, such as diethylenetriaminepentaacetic acid and their alkali metal salts or partial salts. Other chelating agents known in the art can be employed if desired, such as the various polyvalent organic acids, including succinic acid.

The loweralkanol to be employed is any monohydroxyalkane of from 1 to 4 carbon atoms and is represented by methanol, ethanol, normal propanol, isopropanol, and the isomeric butanols. Alkanols of more than 4 carbon atoms manifest diminishing efficacy in the present invention and are not normally used.

The loweralkanolamine to be employed contains 2 to 4 carbon atoms in the alkanol moiety or moieties and from 1 to 3 alkanol moieties per molecule, and is represented by diethanolamine (sometimes called 2,2-iminodiethanol), monoethanolamine, triethanolamine, the mono-, di-, and triisopropanolamines and the homologous loweralkanolamine substances generally.

The loweralkyl ether alcohols are molecules terminated on one end by an alkyl group of from 1 to 4 carbon atoms and may be straight-chain or branched, the other end of such terminal alkyl moiety being ether-bonded through oxygen to another moiety of from 2 to 4 carbon atoms which, being doubly terminated, is called an alkylene moiety, upon the other terminus of which alkylene moiety appears a hydroxyl group e.g. 2-butoxyethanol and 1-methoxy-2-propanol. Results have been incompletely satisfactory when employing any single such loweralkyl ether alcohol and have been satisfactory when employing any mixture of two such substances. More than two can be employed. Each loweralkyl ether alcohol is present in an amount of from 1 to 5 parts per 100 weight parts of total composition.

A representative of each of he tmaterials are combined together in moderate amounts with water, the water being present in an amount substantially greater than the combined amount of all the other ingredients, to obtain a cleaning solution having extraordinary properties in the cleaning of toilet facilities.

More particularly, the chelating agent is supplied in an amount representing from 0.25 to 15 parts and preferably from 1 to 5 parts by weight of 100 parts of total composition. If it is desired to adjust the acidity or alkalinity of the mixture, the chelating agent can be supplied partially as metallic salt and partially as acid.

The loweralkanol is present in from 1 to 5 parts by weight of 100 weight parts of total composition. Each of the loweralkyl ether alcohols is present in substantially similar amount. The alkanolamine is present in from 0.8 to 6 parts by weight of 100 weight parts of total composition with, in each instance, water sufficient to constitute 100 weight parts.

The inventive composition has a pH of from 7 to 12.

It is not to be inferred that a composition lying marginally outside the precise limits here stated would instantaneously give only failing results under use test conditions; but it would be expected to perform less efficaciously.

When desired, such composition can be put into an aerosol can and applied as a spray. Alternatively, it can be applied by a direct pump or propelled by compressed air or by pouring, mopping or swabbing.

Thus, in one aspect, the invention resides in a process which comprises the steps of applying to a soil-bearing toilet surface the aqueous composition described above permitting said composition to remain upon said surface for a period of time sufficient to solubilize at least portions of said soil, and thereafter rinsing the said surface.

As is routine in the cleaning art, the total process of cleaning a toilet surface is rendered easier and usually more effective, if a surface active agent is combined with the cleaning composition above defined. Such surfactant, or soap-like agent, performs its known function. One such function is the reduction of surface tension, formation of micelles, and other routine cleaning functions. Another function which can be performed, when desired, is the exhibition of a composition of the present invention in the form of a foam, either stable or adapted to break and settle as a liquid film reasonably promptly after its application. The application of a composition of this invention in the form of a foam to vertical or under surfaces sometimes offers the advantage of permitting the application of a greater total amount of composition without immediate run-off.

The surfactant material can be any of a wide range of materials. Good results are obtained when employing an anionic surfactant. The alkylbenzene sulfonates are representative, as are the salts of the alkylated, sulfonated diphenyl oxides. Nonionic surfactant materials also give good results, such as ethylene oxide condensation products of alkyl-phenols and diphenyl oxides. Mixtures of the two can be used.

When employed, a surfactant material or mixture of such materials can be employed in the composition in an amount of from 0.1 to 10 weight parts per hundred weight parts of total composition.

When a foam is desired, other foam-forming and, when desired, foam-breaking agents known in the art can be employed.

The pH of a composition according to this invention may vary within relatively wide limits. Most of the chelating agents that will be employed with best results perform most satisfactorily in a pH above 7 but typically, below 12. When a mixture according to the present invention, including water, has been completed, pH can be adjusted, if necessary, by the addition of small amounts of an alkaline substrate to elevate the pH, such a substance as sodium hydroxide. If it is desired to lower the pH from some spontaneously attained value this con be accomplished by the addition of portions of the chelating agent in its acid rather than its salt phase. It is, of course, possible to add one chelating agent in the form of its polyalkali metal salt and employ another, but compatible, chelating agent as an acid to lower pH. Most cleaning compositions are employed in a pH in the range of about 10 to abount 11. That pH gives good results and is the most preferred pH range in most embodiments of the instant invention. This is to be seen in contrast with the employment in the prior art of mineral acid removal of stoney deposits from urine reactions.

When desired, a germicide can be added to a composition of this invention to disinfect or sterilize surfaces. The present invention results in the development of a clean, typically highly polished surface which lends itself almost ideally to being sterilized.

When employing an antimicrobial substance, control of pH of the entire composition may become critical. Many antimicrobial substances are known which perform their function very well at a pH in the range of 3-7 or slightly outside this range but which, at a pH above about 7 to 8 rapidly lose their ability to control at least some kinds of microorganism and perhaps all. Thus, when employing any given germicidal substance for its antimicrobial action in connection with the total cleaning composition of this invention, any given combination should be tested for efficacy after it is prepared. It is not always possible to predict the germicidal activity that may result from such combination upon the basis of the known properties of the isolated subcomponents.

More particularly, a relatively quite versatile antimicrobial substance which has given good result in the present invention over a very wide range of pH values is *o*-phenylphenol. Good results have also been achieved when employing as germicide 4-chloro-2-cyclopentylphenol. In some way that is not fully understood, a combination of these two substances has proved to be efficacious in the disinfestation of toilet premises from total microbiological flora at a rate not reasonably suggested by the known activity of either component alone.

If it is desired to have a foaming composition, it is preferred to employ a propellant which emulsifies under pressure and with shaking. The low-boiling loweralkanes are such substances, including, for example, isobutane. When it is desired to avoid foam, it will be preferred to employ, as propellant, an agent that does not readily emulsify in the composition, and this result can be enhanced by the omission of a surfactant and the employment of, for example, a known halocarbon such as a known fluorohydrocarbon propellant.

One highly satisfactory composition consists of, in weight parts by weight of total composition, 165 parts of the tetrasodium salt of ethylenediamine tetraacetic acid, 34 parts ethylenediamine tetraacetic acid, 300 parts methanol, 250 parts diethanolamine,

300 parts 2-butoxyethanol, 300 parts 1-methoxy-2-propanol, germicide, surfactant, reodorant, and water, sufficient to make 10,000 parts. The term "reodorant" means a substance capable of replacing the previous odour with a more pleasant one.

The following examples illustrates the invention.

EXAMPLE 1

A composition was prepared, employing 164.58 parts of the tetrasodium salt of ethylenediaminetetraacetic acid. To adjust pH to 10.2, 33.83 parts of ethylenediamine tetraacetic acid were added. With it were combined 300 parts methanol, 250 parts diethanolamine, 300 parts 2-butoxyethanol, 300 parts 1-methoxy-2-propanol and 8,047 parts of deionized water. With the admixture of these materials, the composition of the present invention was completed.

However, in order to obtain the improved beneficial results obtained by such further additions, there were added to the foregoing 300 parts of the sodium salt of a dodecylated sulfonated diphenyloxide surfactant and 40 parts orthophenylphenol. Fifteen parts of d-limonene were known to be present (a reodorant substance), and all the foregoing were placed in a can adapted to be employed as a pressurized spray can, and thereinto with the foregoing were introduced 496 parts isobutane as propellant. The can was provided with a valve- and education tube-bearing cap which was crimped into place. As a result of these procedures, there was obtained a can having 12,946.41 parts by weight of content, of the specified composition, adapted to be employed as a pressurized spray can for the application to toilet surfaces of a composition of the present invention.

EXAMPLE 2

The spray can of Example 1 is employed in the cleaning of toilets in a heavily-used industrial toilet facility. Wall-hung urinals and flush toilet bowls are significantly encrusted with urine-originating solids which act as binding agent and detaining agent for other soils; unsightly patches of partially dried fecal matter adhere in places to the adherent urine solids, and, in some of the facilities, microbiological growths of considerable extent have spread over the surfaces of the procelain structures.

Each of the structures is flushed once, to effect momentary cleaning of readily removable substances, and when water flow from the flush has ceased, exposed surfaces and the water pool in each facility are sprayed for a few seconds, long enough to effect an apparent relatively complete but simple coating, with the composition of the pressure spray can described in Example 1.

The composition is permitted to stand for 60 seconds, and each facility is then flushed again. Of the eight fixtures so treated, five are immediately clean to bare and shining clean porcelain, two of which manifest age cracks and thereby deep seated water stains in the porcelain body. The other three show a small remaining residue of various kinds of soil. These are treated again exactly as described hereinbefore, and upon the second flush, are completely cleaned.

WHAT WE CLAIM IS:—

1. An aqueous cleaning composition of a pH of from 7 to 12, comprising a chelating agent in the amount of from 0.25 to 15 parts; a loweralkanol of from 1 to 4 carbon atoms in the amount of from 1 to 5 parts; an alkanolamine of which any alkanol moiety is of from 2 to 4 carbon atoms and there are from 1 to 3 such alkanol moieties per molecule, and the alkanolamine is in the amount of from 0.8 to 6 parts; and a mixture of two or more different loweralkyl ether alcohols of which each is terminated on one end by an alkyl group of from 1 to 4 carbon atoms, ether bonded through oxygen to an alkylene moiety of from 2 to 4 carbon atoms, said alkylene moiety being terminated by a hydroxyl group, each such loweralkyl ether alcohol being present in an amount of from 1 to 5 parts; all amounts being by weight and all parts being by weight of 100 parts of total composition, water being present in amount to complete said composition to 100 weight parts.

2. Composition as claimed in Claim 1 and containing also an anionic surfactant.

3. Composition as claimed in Claims 1 or 2 wherein the chelating agent is selected from nitrilotriacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid and their alkali metal salts.

4. Composition as claimed in any of Claims 1 to 3 wherein the chelating agent is the tetrasodium salt of ethylenediaminetetraacetic acid.

5. Composition as claimed in any of Claims 1 to 4 wherein the loweralkanol is methanol.

6. Composition as claimed in any of Claims 1 to 5 wherein the alkanolamine is diethanolamine.

7. Composition as claimed in any of Claims 1 to 6 wherein the loweralkyl ether alcohol is 2-butoxyethanol.

8. Composition as claimed in any of Claims 1 to 6 wherein the loweralkyl ether alcohol is 1-methoxy-2-propanol.

9. Composition as claimed in any one of the preceding claims wherein the chelating agent is present in amount of at least 2 parts by weight.

10. Composition as claimed in any of claims 1 to 9 and also containing a germicide.

11. Composition as claimed in claim 1 substantially as hereinbefore described in

Example 1.

12. An aqueous cleaning composition comprising in weight parts by weight of total composition, 165 parts of the tetrasodium salt of ethylenediamine tetraacetic acid, 34 parts ethylenediamine tetraacetic acid, 300 parts methanol, 250 parts diethanolamine, 300 parts 2-butoxyethanol, 300 parts 1-methoxy-2-propanol, germicide, surfactant, reodorant, and water, sufficient to make 10,000 parts.

13. Method for cleaning a soil-bearing toilet surface which consists of applying to said surface an at least surface wetting amount of an aqueous composition of a pH of from 7 to 12 comprising a chelating agent in the amount of from 0.25 to 15 parts; a loweralkanol of from 1 to 4 carbon atoms in the amount of from 1 to 5 parts; an alkanolamine of which any alkanol moiety is of from 2 to 4 carbon atoms and there are from 1 to 3 such alkanol moieties per molecule, and the alkanolamine is in the amount of from 0.8 to 6 parts; and a mixture of two or more different loweralkyl ether alcohols of which each is terminated on one end by an alkyl group of from 1 to 4 carbon atoms, ether bonded through oxygen to an alkylene moiety of from 2 to 4 carbon atoms, said alkylene moiety being terminated by a hydroxyl group, each such loweralkyl ether alcohol being present in an amount of from 1 to 5 parts; all amounts being by weight and all parts being by weight of 100 parts of total composition, water being present in amount to complete said composition to 100 weight parts; permitting said composition to remain upon said surface for a period of time sufficient to solubilize at least surface portions of said soil, and thereafter rinsing the said surface.

14. A method as claimed in claim 13 wherein the chelating agent is present in amount of at least 2 parts of the aqueous composition.

15. A method as claimed in claim 13 substantially as hereinbefore described in Example 2.

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